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(54) Stabilizer composition for polymers

(57) A stabilizer composition comprises at least one processing stabilizer selected from special phosphite, mono- and diphosphonite compounds, at least one acid scavenger selected from the group consisting of selected metal stearates, hydrotalcites, oxides and hydroxides, at least one UV stabilizer selected from compounds containing at least one 2,2,6,6-tetraalkylpiperidinyl-group and optionally at least one sterically hindered phenolic antioxidant.

A solid masterbatch composition or a liquid concentrate may comprise the stabilizer composition. A process for stabilizing polymeric materials selected from the group consisting of special polyolefins comprises adding to the polymeric material a stabilizing quantity of the stabilizing composition.

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Stabilizer Composition

This invention relates to a stabilizer composition comprising at least one processing stabilizer selected from special phosphite, mono- and diphosphonite compounds, at least one acid scavenger selected from the group consisting of selected metal stearates, hydrotalcites, oxides and hydroxides of alkaline earth metals, at least one UV stabilizer selected from compounds containing at least one 2,2,6,6-tetraalkylpiperidinyI-group and optionally at least one sterically hindered phenolic antioxidant. The invention relates also to a solid masterbatch composition or a liquid concentrate comprising above-mentioned stabilizer composition. The invention further relates to a process for stabilizing polymeric materials selected from the group consisting of special polyolefins comprising adding to the polymeric material a stabilizing quantity of said stabilizing composition. The invention also relates to stabilized polymeric material comprising said stabilizing composition and the above-mentioned polymeric material.

The rapid progress in the development of polymerization catalysts, especially of supported catalysts and metallocenes, for the manufacture of polyolefins has made a variety of polymers available which differ significantly in their properties from the "early generation" plastics. The problem to maintain these superior properties during processing and service life of the plastic articles has been aggravated especially in polyolefins produced by Generation II to V catalyst systems which are not removed from the polymer after finalizing the polymerization reaction. Even though such catalysts can be deactivated by catalyst poisons, such as steam, aliphatic alcohols, ethers or ketones, their residual activity can still remain to a certain extent. They can attack the polymer and cause premature failures during its end-use; and furthermore, such catalyst residues can also affect the additives which are supposed to safeguard the integrity of plastic materials.

It is well known that several cations with a positive charge ≥ 2 , especially the transition metal ions of the 3d, 4d and 5d series - typical catalysts for olefin polymerization -, can catalyze the decomposition of phosphites and phosphonites,

in particular the hydrolysis of such typical processing stabilizers, finally leading to products with acidic properties and also undesired free phenol. These decomposition products as such can, moreover, cause many disadvantageous secondary effects; for example, negative interactions with other additives, especially hindered amine UV stabilizers or phenolic antioxidants, eventually disturbing the entire balance of the additive system contained. In consequence thereof, problems can become apparent already during melt processing of the polymer, e.g. in form of gel particles, various kinds of deposits or black specks, as well as during its service life, e.g. as reduced mechanical properties, surface cracks or premature embrittlement when the polymer is exposed to daylight and climate influences.

Many of these undesired processes in a polymeric matrix have been found to originate from a certain acidity, originally present or later formed during the lifetime of a polymer. Therefore, sufficient amounts of acid scavengers, such as metal stearates or oxides, are added to overcome the aforementioned problems. One of the most widely used acid scavengers is calcium stearate, typically used in concentrations of 0.03 - 0.15%.

However, several other undesired processes, which cannot directly be correlated with the formation of acidity have been observed in a polymeric matrix despite the presence of acid scavengers. Although the details of such reactions or mechanisms are not fully understood, the consequences thereof can become clearly visible. For instance, certain combinations of plastic additives appear to show negative interactions, often expressed as reduced overall performance, compared with the individual effects of the single additives applied alone in the same polymer.

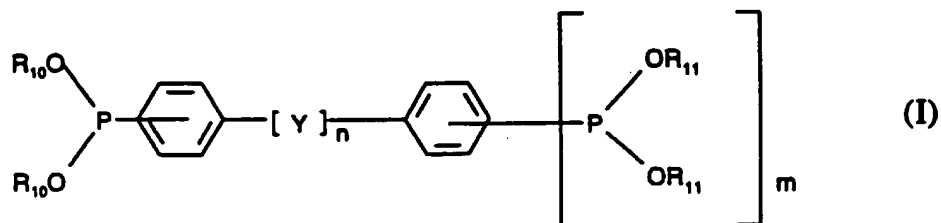
One example for such negative interactions is the simultaneous use of certain processing stabilizers, e.g. Sandostab® P-EPQ or Irgafos® 12, together with sterically hindered amines (HALS) in UV stabilized polyolefins. Both types of additives are commercially, respectively from a technical viewpoint, important products and essential for the use in high performance plastics. The phosphorus

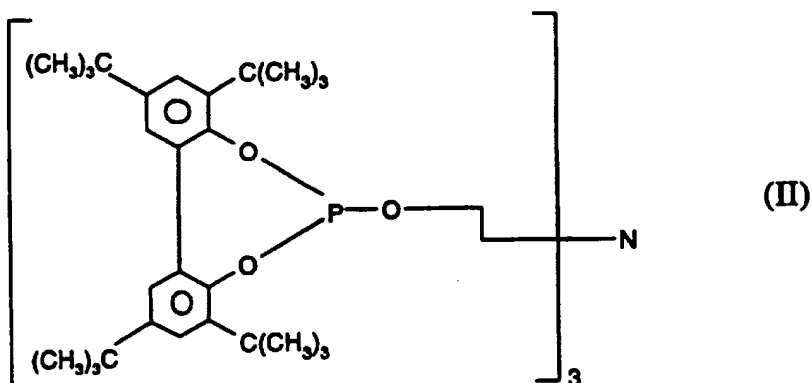
compounds are known to exceptionally safeguard the integrity of the polymer during melt processing; HALS compounds are the state-of-the-art stabilizers to protect polyolefins against the detrimental influence of UV light. However, these two types of additives are known to interact antagonistically and therefore, it has been explicitly recommended not to use any combinations thereof (see publication of Dr. W.O. Drake of Ciba-Geigy, Basel in "Plastics News", April 1989, pages 36-45). In particular, the efficiency of HALS as UV stabilizer is said to be drastically reduced in such cases, limiting the industrial use of such combinations significantly.

It is the objective of the invention to solve the above-mentioned problems and to provide a high performance stabilizer composition for the stabilization of polyolefins, in particular those which are produced by Generation II to V [and higher] catalyst systems which are not removed from the polymer after the polymerization reaction.

In accordance with the present invention said problem is solved by a stabilizer composition comprising

- a) at least one processing stabilizer selected from the group consisting of phosphite, monophosponite and diphosponite compounds of formula I or II





in which

m is 0 or 1;

n is 0 or 1;

each R_{10} and each R_{11} , independently, is an aliphatic, alicyclic or aromatic group of C_{1-24} carbon atoms, optionally further substituted (for example by linear or branched aliphatic groups or alkaryl substituents) (hereinafter defined as the monovalent significances of R_{10} or R_{11} , respectively);

or both groups R_{10} and/or R_{11} form a cyclic group with a single phosphorus atom (hereinafter defined as the divalent significances of R_{10} or R_{11} , respectively);

Y is $-O-$, $-S-$, $-CH(R_{15})-$ or $-C_6H_4-$,

where R_{15} is hydrogen or C_{1-8} alkyl or $COOR_6$ and R_6 is C_{1-8} alkyl.

- b) at least one acid scavenger selected from the group consisting of sodium stearate, magnesium stearate, zinc stearate; magnesium or magnesium/zinc hydrotalcites, optionally coated with 5 to 50% of metal stearate; zinc oxide, zinc hydroxide, calcium oxide, calcium hydroxide, magnesium oxide,

magnesium hydroxide.

- c) at least one UV stabilizer selected from compounds containing at least one 2,2,6,6-tetraalkylpiperidinyl-group

and

- d) optionally at least one sterically hindered phenolic antioxidant selected from the group consisting of octadecyl3-(-3',5'-di-tert.-butyl - 4'-hydroxyphenyl)propionate, tetrakis [methylene-3-(3',5'-di-tert.-butyl-4'-hydroxyphenyl) propionate] methane, 1,3,5-trimethyl-2,4,6-tris(3,5-di-tert.butyl-4-hydroxyphenyl)benzene, 1,3,5-tris(3,5-di-tert.-butyl-4-hydroxyphenyl)-1,3,5-triazine-2,4,6-(1H,3H,5H)trione and tris[3,5-di-tert.-butyl-4-hydroxybenzyl]isocyanurate.

According to the invention, there is provided a synergistic additive package, i.e. a stabilizer composition for polyolefins, in which highly effective processing stabilizers and hindered amine UV stabilizers are combined without sacrificing the individual effects of the additives contained. The selected acid scavengers are able to compensate the negative interactions of processing stabilizers and HALS compounds. In some cases, even superior efficiency of the HALS compounds has been observed, compared with analogous formulations containing such processing stabilizers, which do not show such negative interactions.

Preferably in component a) the monovalent significances of R_{10} and R_{11} are independently linear, branched or cyclic C_{1-24} aliphatic groups; or aromatic groups, e.g. phenyl, preferably substituted 1 to 5 fold with C_{1-12} alkyl or aralkyl groups, as for example with $R_{10} = R_{11} = 2,4$ -di-tert-butyl phenyl.

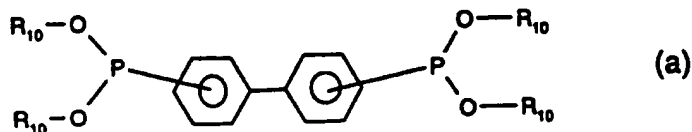
The weight ratio of component a) to b) in the stabilizer composition according to the invention is preferably 3:1 to 1:7, more preferably 2:1 to 1:2.

The typical ratios of components a) to d) are 1:5 to 5:1, preferably in the range of 1:3 to 3:1. The amount of component c), relative to the sum of components a) plus b) plus d), may vary from 1:100 to 100:1, preferably however from 1:20 to 20:1.

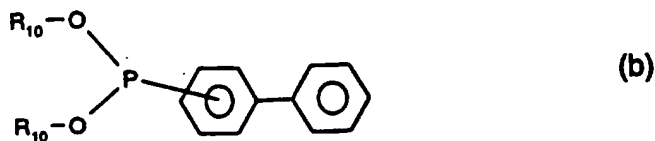
The synergistic additive package comprising the components a), b), c) and d) is preferably used in polymers at concentrations of 0.05 to 2%, more preferably at 0.1 to 1%.

Component a) is preferably a compound being a mixture of

- i) 50-80% of a diphosponite of the formula (a)



- ii) 5-25% of a monophosponite of formula (b)



- iii) 5-25% of a phosphite of formula (c)

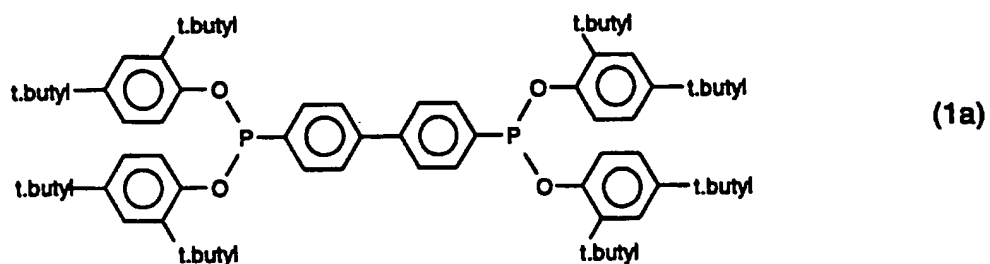


in which each R_{10} is 2,4-di-tertiary butyl phenyl; and where the percentages are weight percentages (based on the sum of the compounds of formulae

(a), (b), and (c) being 100%).

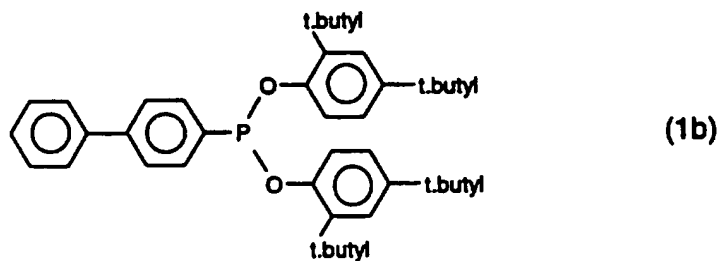
More preferably component a) is a product by process composed of:

- i) 60 - 65 parts of the diphosphonite of formula 1a



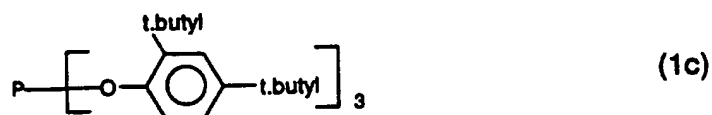
(tetrakis (2,4-di tert. butylphenyl) biphenylene diphosphonite)

- ii) 10 - 15 parts of the monophosphonite of formula 1b



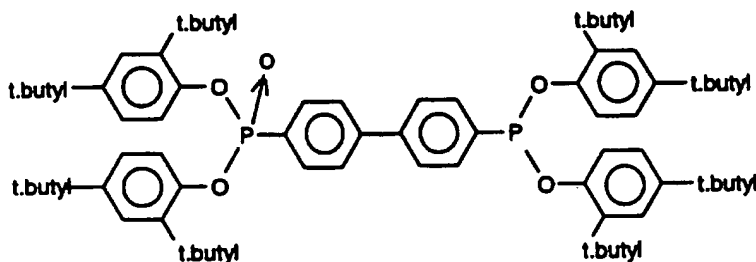
(bis (2,4-di-tert. butylphenyl) biphenylene monophosphonite)

- iii) 10 - 15 parts of the phosphite of formula 1c



(tris (2,4-di-tert. butylphenyl) phosphite)

- iv) up to 3.5 parts of 2,4 di tert. butyl phenol;
- v) up to 1% of inorganic chloride;
- vi) up to 0.5% of volatile matters;
- vii) up to 5% of a compound of the formula

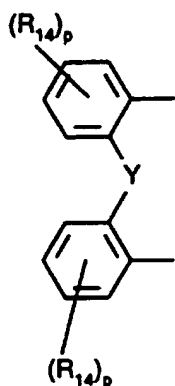


This mixture of components i - vii is commercially available as Sandostab® P-EPQ from CLARIANT International, LTD, Switzerland.

In component a), the compound of formula II, chemically characterized as 2,2',2''-nitriolo[triethyl-tris(3,3',5,5'-tetra-tert. butyl-1,1'-biphenyl-2,2'-diyl)phosphite], can be applied as obtained by the procedure given in Example 4 of US Patent 4,318,845, respectively Example 4 of US Patent 4,374,219, with a melting range of 121-134°C, or in its amorphous solid form with a melting range of 105-110°C according to US

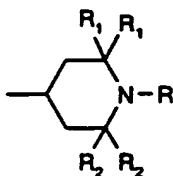
Patent 5,276,076, or in its triclinic β -modification with a melting range of 200-207°C according to US Patent 5,326,802, or in its γ -modification with a melting range of 178-185°C according to US Patent 5,331,031, or in its monoclinic α -modification with a melting range of 145-165°C according to US Patent 5,334,739, in mixtures, melts or in solutions thereof.

Preferably the divalent significances of R_{10} and R_{11} are e.g.



where each R_{14} independently is selected from C_{1-22} alkyl or C_{7-22} aralkyl and $p = 0$ to 4, preferably 1 to 3.

The 2,2,6,6-tetraalkylpiperidiny-group of component c) is of formula α)



α)

in which

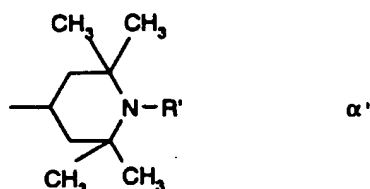
R is hydrogen; oxygen; -OH; C₁₋₂₄alkyl; -O-C₁₋₂₄alkyl; -O-CO-C₁₋₂₄alkyl; -O-CO-phenyl or -COR₅; where R₅ is -C(R₃)=CH₂, C₁₋₆alkyl, phenyl, CO-C₁₋₂₄alkyl, -CO-phenyl, -NR₇R₈, -CH₂-C₆H₅, -CO-OC₁₋₁₂alkyl or -COOH; R₃ is hydrogen or C₁₋₄alkyl; R₇ is hydrogen, C₁₋₁₂alkyl, C₅₋₈cycloalkyl, phenyl, phenyl-C₁₋₄alkyl or C₁₋₁₂alkylphenyl and R₈ is C₁₋₁₂alkyl or hydrogen,

each R₁, independently, is -CH₃ or -CH₂(C₁₋₄alkyl) or both groups R₁ form a group -(CH₂)₅-; and

each R₂, independently, is -CH₃ or -CH₂(C₁₋₄alkyl) or both groups R₂ form a group -(CH₂)₅-.

Such a group of formula α) is known as the effective group in numerous Hindered Amine Light Stabilizers (HALS).

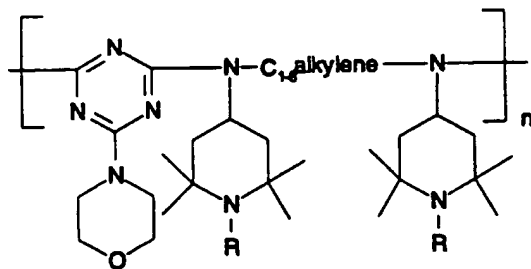
More preferably component c) is a compound containing a group of formula α'



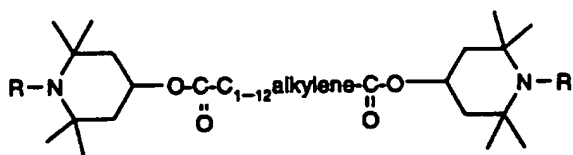
where R' is hydrogen, oxygen, OH, C₁₋₁₂alkyl, O-C₁₋₁₂alkyl or -CO-C₁₋₈alkyl.

Preferably component c) is selected from HALS 1 to HALS 18 below

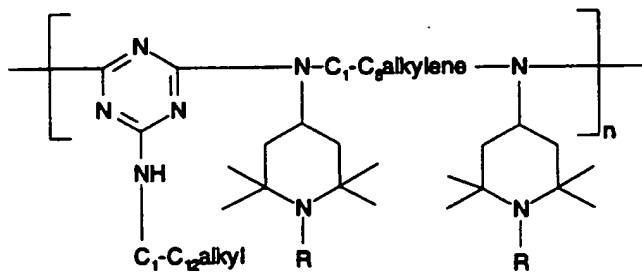
HALS 1



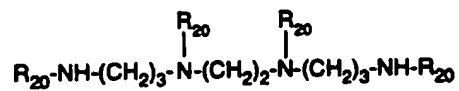
HALS 2



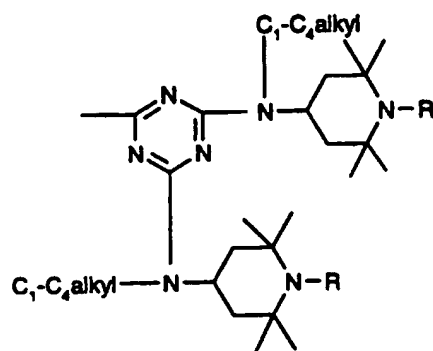
HALS 3



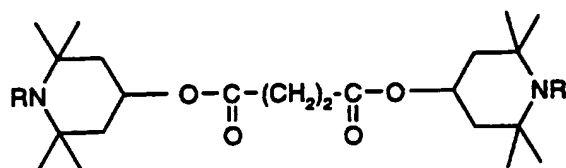
HALS 4



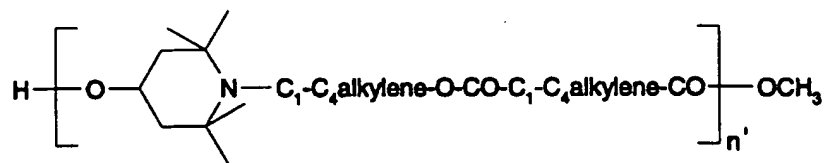
where R_{20} is



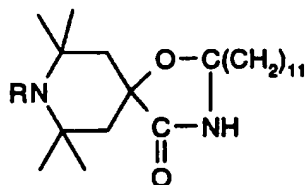
HALS 5



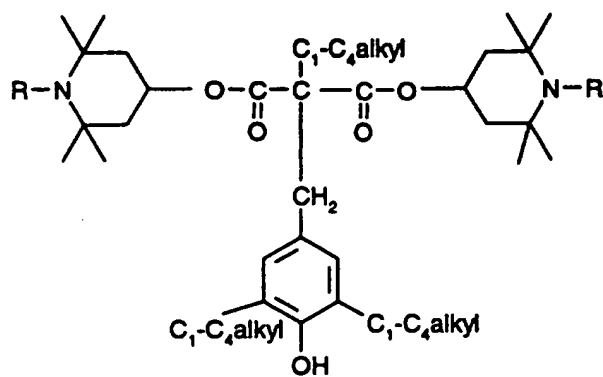
HALS 6



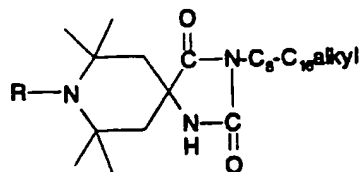
HALS 7



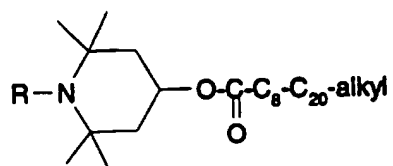
HALS 8



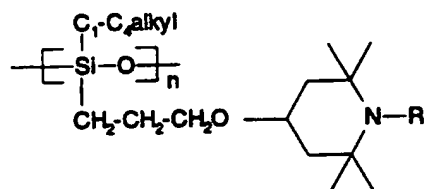
HALS 9



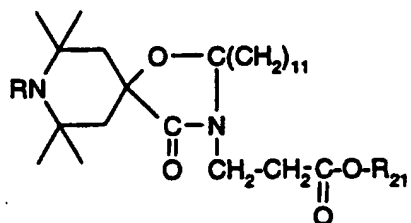
HALS 10



HALS 11

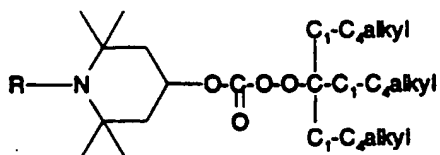


HALS 12

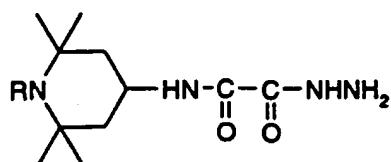


where R_{21} is C_{12-14} alkyl (e.g. a mixture of $C_{12}H_{25}$ and $C_{14}H_{29}$);

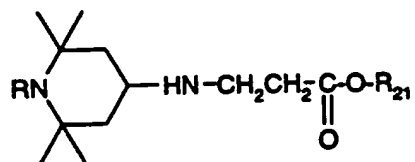
HALS 13



HALS 14

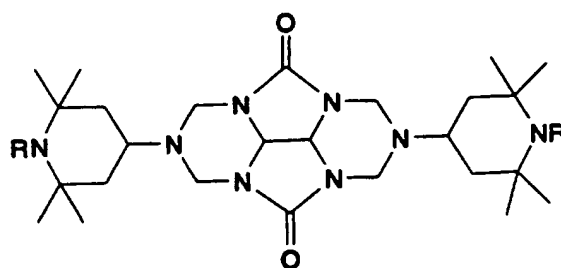


HALS 15

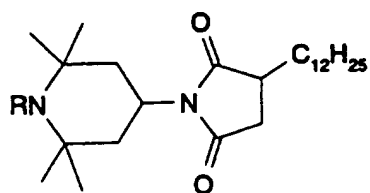


where R₂₁ is as defined above

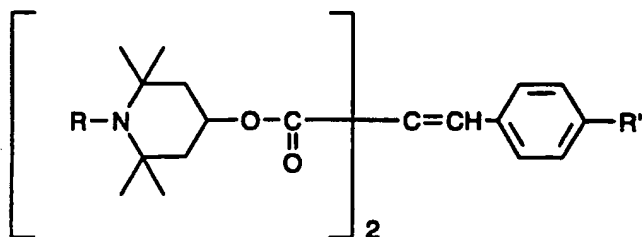
HALS 16



HALS 17



HALS 18



in which in **HALS 1** to **HALS 18**

R is R' where R' is hydrogen, oxygen, OH, C₁₋₁₂alkyl, O-C₁₋₁₂alkyl or -CO-C₁₋₈alkyl and

n' is a number from 3 to 20.

Most preferably component c) is selected from:

Bis (2,2,6,6-tetramethyl-4-piperidyl) sebacate;

Bis(1,2,2,6,6-pentamethyl-4-piperidiny)(3,5-ditert.

butyl-4-hydroxybenzyl)butylpropane dioate;

Bis (1,2,2,6,6-pentamethyl-4-piperidiny) sebacate;

8-Acetyl-3-dodecyl-7,7,9,9-tetramethyl-1,3,8-triazaspiro(4,5)decane -2,4-dione;

Butanedioic acid, bis(2,2,6,6-tetramethyl-4-piperidiny) ester;

Tetrakis (2,2,6,6-tetramethyl-4-piperidyl)-1,2,3,4-butane tetracarboxylate;

(2,2,6,6-tetramethyl-4-piperidyl)/β,β,β',β'-tetramethyl-3,9-(2,4,8,10-tetra-oxaspiro(5',5)undecane) diethyl)-1,2,3,4-butane tetra carboxylate;

7-oxa-3,20-diazadispiro(5.1.11.2)heneicosan-20-propanoic acid, 2,2,4,4-tetramethyl- 21-oxo, dodecylester ("Hostavin" N 24);

Octadecene-(N-(2,2,6,6-tetramethylpiperidiny-4)-N-maleinimido-oxalic acid diamide

co-polymer;

N-(2,2,6,6-tetramethyl-4-piperidiny)-N'-amino-oxamide;

OO-t-amyl-O-(1,2,2,6,6-pentamethyl-4-piperidiny)monoperoxycarbonate;

β -Alanine-N-(2,2,6,6-tetramethyl-4-piperidiny)-dodecylester;

Ethanediamide,N-(1-acetyl-2,2,6,6-tetramethylpiperidiny)-N'-dodecyl;

3-dodecyl-1-(2,2,6,6-tetramethyl-4-piperidiny)-pyrrolidin-2,5-dione;

3-dodecyl-1-(1,2,2,6,6-pentamethyl-4-piperidiny)-pyrrolidin-2,5-dione;

3-dodecyl-1-(1-acetyl,2,2,6,6-tetramethyl-4-piperidiny)-pyrrolidin-2,5-dione;

("Sanduvor[®]" 3058)

4-benzoyloxy-2,2,6,6-tetramethylpiperidine;

1-[2-(3,5-di-tert.butyl-4-hydroxyphenylpropionyloxy)ethyl]-4-(3,5-ditert.-

butyl-4-hydroxy-phenyl-propionyloxy)-2,2,6,6-tetramethyl piperidine;

2-methyl-2-(2'',2'',6'',6''-tetramethyl-4''-piperidinylamino)-N-(2',2',6',6'-tetra-methyl-4'-piperidiny) propionylamide;

1,2-bis(3,3,5,5-tetramethyl-2-oxo-piperaziny)ethane-1-isopropyl-3,3,5,5-tetramethyl-2-piperazinone

Tetrakis (2,2,6,6-tetramethyl-4-piperidyl) 1,2,3,4-butane tetracarboxylate;

4-oleoyloxy-2,2,6,6-tetramethylpiperidine;

Poly-[(6-morpholino-s-triazin-2,4-diyl)((2,2,6,6-tetramethyl-4-piperidiny)imino)-hexamethylene-((2,2,6,6-tetramethyl-4-piperidiny)imino)];

Poly-[6-[1,1,3,3-tetramethyl-butyl)imino]-s-triazin-2,4-diyl][2-(2,2,6,6-tetramethyl-4-piperidiny)imino]hexamethylene-[4-(2,2,6,6-tetramethyl-4-piperidiny)imino)];

1,3,5-triazine-2,4,6-triamine-N',N''-[ethanediyl-bis[[[4,6-bis[butyl(1,2,2,6,6-pentamethyl-4-piperidiny)amine]-1,3,5-triazin-2-yl]imino]propane-diyl]]bis[N',N''-dibutyl-N',N''-bis-(1,2,2,6,6-pentamethyl-4-piperidiny)];

Butanedioic acid, polymer with 4-hydroxy-2,2,6,6-tetramethyl-1-piperidine-ethanol;

2,2,4,4-tetramethyl-7-oxa-3,20-diaza-dispiro[5.1.11.2]heneicosan-21-one;

Bis(1-octyloxy-2,2,6,6-tetramethyl-4-piperidiny)sebacate;

Poly(methylpropyl-3-oxy-[2,2,6,6-tetramethyl-4-piperidiny]-siloxane);

1,3,5,7,9,11-hexaaza-4,10-dione-tricyclo[12.1.1.013,14]-tetradecane-1,7-bis(2,2,6,6-tetramethyl-4-piperidiny).

Especially useful as component c) are

Bis (2,2,6,6-tetramethyl-4-piperidyl) sebacate;

Bis (1,2,2,6,6-pentamethyl-4-piperidiny) sebacate;

Butanedioic acid, bis(2,2,6,6-tetramethyl-4-piperidiny) ester;

Poly-[(6-morpholino-s-triazin-2,4-diyl)[(2,2,6,6-tetramethyl-4-piperidiny)imino]-hexamethylene-[(2,2,6,6-tetramethyl-4-piperidiny)imino)];

Poly-[6-[1,1,3,3-tetramethyl-butyl)imino]-s-triazin-2,4-diyl][2-(2,2,6,6-tetramethyl-4-piperidiny)imino]hexamethylene-[4-(2,2,6,6-tetramethyl-4-piperidiny)imino)];

1,3,5-triazine-2,4,6-triamine-N',N''-[ethanediyl-bis[[[4,6-bis[butyl(1,2,2,6,6-pentamethyl-4-piperidiny)amine]-1,3,5-triazin-2-yl)imino]propane-diyl]]bis[N',N''-dibutyl-N',N''-bis-(1,2,2,6,6-pentamethyl-4-piperidiny)];

Butanedioic acid, polymer with 4-hydroxy-2,2,6,6-tetramethyl-1-piperidine-ethanol;

Bis(1-octyloxy-2,2,6,6-tetramethyl-4-piperidiny)sebacate;

Poly(methylpropyl-3-oxy-[2,2,6,6-tetramethyl-4-piperidiny]-siloxane)

Further, component c) can optionally be combined with known UV absorbers.

Components a) to c) and optionally d) of the stabilizer composition according to the invention can be added individually to the polymeric materials to be stabilized or can be blended to form an additive package, prior to the addition to the polymeric material. This additive package can be prepared by mixing the components a) to c) and optionally d) in an appropriate mixer to obtain a powder blend which preferably is compacted to non-dusting granules by known methods.

Another possibility to prepare such additive packages is to prepare a homogeneous melt of the components a) to c) and optionally d) at elevated temperatures which is then cooled and pelletized by known methods.

Further additives that can be added to a composition according to the invention include antioxidants as well as UV absorbers (e.g. 2-(2'-hydroxyphenyl)-benztriazoles, 2-hydroxy-benzophenones, 1,3-bis-(2'-hydroxybenzoyl) benzene, salicylates, cinnamates and oxalic acid diamides; UV quenchers such as benzoates

and substituted benzoates, antistatic agents, flameproofing agents, lubricants, plasticisers, nucleating agents, metal deactivators, biocides, impact modifiers, fillers, pigments and fungicides.

Further according to the invention there is provided a solid masterbatch composition or liquid concentrate for use as a stabilizer in polymeric materials. Said masterbatch composition comprises 10 to 80% by weight, preferably 15 to 40% by weight, of a stabilizer composition according to the invention and 90 to 20% by weight, preferably 85 to 60% by weight, of a polymeric material which is identical or compatible with the polymeric material to be stabilized.

The liquid concentrate comprises 10 to 80% by weight of a stabilizer composition according to the invention and 90 to 20% by weight of a solvent.

A further subject matter of the invention is a process for stabilizing polymeric materials comprising adding to the polymeric material a stabilizing quantity of the stabilizing composition or of the solid masterbatch or of the liquid concentrate according to the invention. This stabilizing quantity is as aforementioned related to the polymeric materials to be stabilized, independent of the selected addition technique.

The stabilizing composition or the masterbatch composition according to the invention may be incorporated by known methods into the polymeric material to be stabilized. Of particular importance is the dry-blending with the polymeric material or coating shaped polymer particles, e.g. polymer spheres, with the present compositions in the form of a liquid, a solution or a suspension/dispersion.

Of particular importance is the blending of the stabilizing composition or the masterbatch composition according to the invention with the polymeric material to be stabilized in the melt, for example in a melt blender or during the formation of shaped articles, including films, tubes, fibres and foams by extrusion, injection

moulding, blow moulding, spinning or wire coating.

The polymeric material to be stabilized according to the invention is selected from the group consisting of homopolyolefins and copolyolefins produced in the presence of a so-called generation II or higher catalyst (not subjected to a catalyst removal step after the polymerization process), and mixtures or blends thereof or with other polymers.

Preferably the polyolefin is selected from the group consisting of homopolypropylene, copolypropylene, homopolyethylene, copolyethylene and mixtures or blends thereof or with other polymers.

Said poly- and copolyolefins are especially prepared using processing catalysts known as Generation II to Generation V catalysts and which have not been subjected to a catalyst removal step. By the term "catalyst removal step" used herein is meant a step for the purpose of positively removing the catalyst residues contained in the polymerized polyolefins or treating the polyolefins with the compound which can react with the catalyst residue and inactivate or solubilize the residue, such as alcohols or water, and then removing the inactivated or solubilized catalyst residue by physical means such as filtration, washing and centrifuging. Thus, in the case of suspension polymerization, the step of separating the resulting polymer from a dispersion medium, such as a solvent or a liquified monomer, does not fall under the above-mentioned definition of the "catalyst residue removal" step, although the catalyst dissolved in the dispersion medium may be removed by a separation step.

The step of adding a small amount of catalyst poisons such as ethers, alcohols, ketones, esters and water to the resulting polymer, to inactivate the catalyst remaining after the completion of polymerization, or the step of treating the resulting polymer suspension with gas such as air or nitrogen to remove the dispersion medium also does not fall under the above-mentioned definition of the

"catalyst residue removal" step.

What we mean by Generation I catalysts are titanium halide catalysts and an organo aluminium compound or an organo aluminium halide.

What we mean by Generation II catalysts are Generation I catalysts supported on an organo magnesium compound or based on an organo chromium compound supported on SiO_2 .

What we mean by a Generation III catalyst is a Ziegler type complex catalyst supported on a halogen containing magnesium compound.

What we mean by a Generation IV catalyst is a Generation III catalyst with a silane donor.

What we mean by Generation V catalysts is a bis-indenyl organo titanium compound supported on alumoxane or bis cyclopentadienyl titanium halides activated by aluminium alkyl compound.

Further generations of highly specific catalysts, especially useful for manufacturing highly stereoregular poly- α -olefins, which are presently under development, belong to the aforementioned generations of supported catalyst systems. Examples for the microstructure of such highly stereoregular polyolefins are syndiotactic polypropylene, isotactic stereoblock polymers, isotactic polypropylene containing stearic defects randomly distributed along the polymer chain (so called anisotactic polypropylene) or stereoirregular stereoblock polymers. Reviews of the most recent developments in the field of metallocene based catalyst systems are: W.N. Riss and H. Ledwinka: *Kunststoffe* 83 (1993) 8, pages 577-583; R. Mülhaupt: *Nachr. Chem. Tech. Labs* 41 (1993) 12, pages 1341-1351; R. Leaversuch: *Modern Plastics*, October 1991, pages 46-49 and W. Spaleck: *Hoechst High Chem Magazine* 14 (1993), pages 44-48. Due to the rapid progress in the development of

newer generation catalyst systems, the commercial significance of these polymers with novel, highly interesting properties is increasing.

These generations of catalysts are also described in the Twelfth Annual International Conference on Advances in the Stabilization and Controlled Degradation of Polymers held in Luzern, Switzerland, 21-23 May 1990 in an article on pages 181 to 196 inclusive by Rolf Mülhaupt entitled "New Trends in Polyolefin Catalysts and Influence on Polymer Stability". The contents of this article is incorporated herein by reference and especially Table I on page 184 describing the Generation of Catalysts:

TABLE I Polyolefin Catalyst Evolution

Generation	Example	Cat.Act. (g/PP/gTi)	% Act.Ti (h atm)	Stereoreg. (% insol in heptane)	Process Technology
I.	TiCl ₄ /AlR ₃	40	0.01	45%	removal of cat.residues and atactic PP
	TiCl ₃ /AlEt ₂ Cl	30	0.1	92%	removal of catalyst residues
II	Mg(OEt ₂)/TiCl ₄ /AlR ₃ SiO ₂ /Cp ₂ Cr	40000 40000	HDPE	50%	no removal of cat.residues (mainly HDPE/LLDPE)
III	Mod.TiCl ₃ cat. MgCl ₂ /TiCl ₄ /AlR ₃ + ester donor	5000 20000	1 10	95% 92%	no purification
IV	MgCl ₂ /TiCl ₄ /AlR ₃ + silane donor	40000	18	99%	no purification no extrusion
V	Bis-indenyl-TiR ₂ on (AlCH ₃ O) _x	40000	100	99%	novel PPs, narrow MWD

in which R is an organo group; HDPE is high density polyethylene, LLDPE is linear low density polyethylene, Cp is cyclopentadienyl, Et is ethyl, PP is polypropylene, MWD is molecular weight distribution and x is an integer above 2 (preferably 2-100).

The invention relates also to a stabilized polymeric material comprising

a) a stabilizing composition according to the invention,

and

b) a polymeric material selected from the group consisting of homopolyolefins and copolyolefins, preferably selected from the group consisting of homopolypropylene, copolypropylene, homopolyethylene, copolyethylene produced in the presence of a so-called generation II or higher catalyst and mixtures or blends thereof or with other polymers.

Further, in this specification, where a range is given, the figures defining the range are included therein. Any group capable of being linear or branched is linear or branched unless indicated to the contrary.

For the avoidance of doubt, in this specification t.butyl means tertiary butyl, $(-C(CH_3)_3)$.

The invention will now be illustrated by the following Examples in which all parts and percentages are by weight unless indicated to the contrary.

EXAMPLES

All examples are carried out with polymeric materials produced with catalysts of the 2nd or higher generation, not subjected to a catalyst removal step. The preparation of the samples is performed in the following manner:

Powdery polymer is dry blended in a mixer with all additives according to the respective compositions. Then, the blend is melt processed on a single screw lab extruder at 210-220°C to manufacture pelletized polymer with a homogeneous distribution of the additives. These pellets are used to prepare polymer films by compression or blow molding or to manufacture fibers on commercially available processing equipment. The UV stability of the finished plastic specimens is tested with an Atlas Weatherometer WOM 65 WRC (artificial weathering) at 63°C black panel

temperature applying either the CAM 7 exposure of 102 min dry/18 min wetting cycles or just dry exposure without artificial rain during the continuous Xe arc irradiation. For UVA exposure tests, UVCon equipment is used. Depending on the applications, the criteria for failure of the samples are 50% reduction of mechanical properties, e.g. tensile strength or elongation at break, and/or the increase of the Carbonyl Index to value of 0.3 versus the unexposed reference.

In the examples the following trade names are used:

- | | |
|-------------------|--|
| Irganox® 1010: | this is an antioxidant on the basis of a sterically hindered phenol available from Ciba-Geigy, Switzerland |
| Sanduvor® 3944: | this is an oligomeric HALS of high molecular weight, available from CLARIANT International, Switzerland |
| Sandostab® P-EPQ: | a compound consisting of the components (i) to (vii), as described before, available from CLARIANT International, Switzerland |
| Irgafos® 12: | a compound available from Ciba-Geigy which is 2,2',2''-nitrido[triethyl-tris(3,3',5,5'-tetra-tert. butyl-1,1'-biphenyl-2,2'-diyl)phosphite] |
| Irgafos® 168: | a compound available from Ciba-Geigy which is tris (2,4-di-tert-butylphenyl)phosphite |
| Irganox® 3114: | a compound available from Ciba-Geigy which is tris[3,5-di-tert.-butyl-4-hydroxybenzyl]isocyanurate |
| L-55 R: | hydrotalcite, a magnesium aluminium hydroxide carbonate hydrate, coated with 18% sodium stearate, available from Reheis Inc, Berkeley Heights, NJ, USA |
| Hysafe 510: | a magnesium hydrotalcite, available from J. M. Huber Corp., Havre de Grace, MD, USA |
| Ultrinox 626: | a commercial phosphite processing stabilizer of G.E. Speciality Chemicals |

In the examples the following abbreviations are used:

ZnSt₂:	Zinc stearate
CaSt₂:	Calcium stearate
NaSt:	Sodium stearate
I-168:	Irgafos® 168
I-12:	Irgafos® 12
P-EPQ:	Sandostab® P-EPQ
WOM:	Weatherometer
COI:	Carbonyl Index
t_f:	time to failure (by COI)
U 626:	Ultranox 626
H-510:	Hysafe 510
ZnO:	Zinc oxid
t₅₀:	time to failure by 50% loss of the original tensile strength

Example 1

Specimens:	Films of 100 µm thickness made by compression molding of polypropylene homopolymer having a MFI (230°C, 2.16 kg) of 1.8 g/10 min
UV Exposure:	Atlas WOM 65 WRC under CAM 7 conditions
Test Criteria:	Time to failure by COI = 0.3, designated as "t_f"
Formulations:	All samples are base stabilized with 0.05% Irganox® 1010 and 0.15% Sanduvor® 3944 (HALS compound). They contain the further additives as listed below

No.	Further Additives	t _i	Relative
A)	0.07% I-168 0.01% CaSt ₂	2210 h	100%
B)	0.07% P-EPQ 0.10% CaSt ₂	1825 h	83%
C)	0.07% I-168 0.10% NaSt	1920 h	87%
D)	0.07% P-EPQ 0.10% NaSt	2520 h	114%

The comparison between formulations A) and B) illustrate the efficiency reducing effect of Sandostab® P-EPQ versus Irgafos® 168 on the UV stabilization of polypropylene, observed for the HALS compound Sanduvor® 3944. This also confirms analogous data of the scientific literature as cited. If the acid scavenger calcium stearate, as used in formulations A) and B), is replaced with sodium stearate, the new formulation D) was found to surprisingly overcome this disadvantage of the Sandostab® P-EPQ combination with HALS. Even a 14% superior effectiveness of the HALS was found in comparison to the reference formulation A). Comparative example C), shows, furthermore, that the beneficial use of sodium stearate gives unique advantages only with Sandostab® P-EPQ and HALS as described, however, not with the Irgafos® 168 processing stabilizer.

Example 2

The specimens, formulations and test criteria are identical with those given in Example 1. However, the exposure tests were carried-out under more severe conditions in an UVCon UVA weathering equipment. This comparison to Example 1 should illustrate that the same rank order of stabilization effects is observed, independent of the kind of test conditions selected.

No.	Further Additives	t_f	Relative
A)	0.07% I-168 0.01% CaSt ₂	1715 h	100%
B)	0.07% P-EPQ 0.10% CaSt ₂	980 h	57%
C)	0.07% I-168 0.10% NaSt	1390 h	81%
D)	0.07% P-EPQ 0.10% NaSt	1770 h	103%

These experimental results confirm the superiority of the unique formulation D) according to the invention over the reference A) and underline the data of Example 1. The application of sodium stearate neutralizes selectively the observed negative interaction of Sandostab® P-EPQ and HALS.

Example 3

Specimens: Compression molded films of polypropylene homopolymer with a thickness of 100 µm, a typical grade for film and sheet extrusion having a MFI (230°C, 2.16 kg) of 1.8 g/10 min

UV Exposure: Atlas WOM 65 WRC under CAM 7 conditions

Test Criteria: Time to failure by COI = 0.3, designated as " t_f "

Formulations: All samples contain 0.05% Irganox® 1010, 0.10% Sanduvor® 3944 and 0.07% Sandostab® P-EPQ plus further additives as listed below

No.	Further Additives	t_f	Relative
A)	0.1% CaSt ₂	1233 h	100%
B)	0.1% NaSt	1588 h	126%
C)	0.5% NaSt	1500 h	121%
D)	0.0% NaSt	1067 h	87%

The above examples indicate again the benefits of sodium stearate over calcium stearate in formulations comprising Sandostab® P-EPQ combinations with HALS compounds (the presence of the phenolic antioxidant Irganox® 1010 is optional and not very significant for the UV stability). If no stearate is used at all, the efficiency of the formulation D) becomes even inferior to the reference A) of this series. It is obvious from the data given in Examples 1 and 3 that preferred concentrations of the sodium stearate neutralizer are defined by specific ratios of Sandostab® P-EPQ/NaSt from 3/1 to 1/7, most preferred in the range of 2/1 to 1/2 to provide optimally balanced stabilization of the polymer.

Example 4

Specimens: A typical polypropylene reactor grade having a MFI (230°C, 2.16 kg) of 12 g/10 min was used to manufacture 160/14 dtex multi-filaments

UV Exposure: Atlas WOM 65 WRC under DRY conditions

Test Criteria: Time to failure by 50% loss of the original tensile strength

Formulations: All samples are base stabilized with 0.05% Irganox® 3114 and 0.20% Sanduvor® 3944 plus further additives as listed below

No.	Further Additives	t ₅₀	Relative
A)	0.08% I-168 0.06% CaSt ₂	551 h	100%
B)	0.08% P-EPQ 0.06% CaSt ₂	493 h	89%
C)	0.08% P-EPQ 0.06% L-55R	733 h	133%
D)	0.08% P-EPQ 0.06% H-510	613 h	111%
E)	0.08% P-EPQ 0.06 MgSt ₂	585 h	106%

The above examples illustrate that the invention can equally be applied on additive formulations for use in UV stabilized PP fibers. Whereas the presence of calcium stearate is not suitable to neutralize the negative interaction of Sandostab® P-EPQ with the HALS compound (which is never observed in similar formulations containing Irgafos® 168 instead, see comparative Example 4A), some other acid scavengers were found to be capable to overcome this antagonism also in this application. In this way, it has become possible to utilize the benefits of superior melt and color stability of the polymer by the use of Sandostab® P-EPQ and optionally a phenolic antioxidant, without detracting from the efficient UV stabilization of the polymer, achieved by the use of the HALS compound. Among the above formulations listed, No. C) is certainly the most preferred combination comprising Sandostab® P-EPQ and L-55R. Also examples D) and E) have significance over the comparative examples A) and B). It should be recognized, furthermore, that the use of the coated version of the hydrotalcite L-55R is preferred over the uncoated form H-510. Both products are again superior to combinations of the magnesium stearate with Sandostab® P-EPQ, i.e. the preferences in the above formulations can be rank-ordered as E) < D) < C), all clearly exceeding the comparative examples A) and B). Only the commonly used calcium

stearate (formulation B) is not applicable (see also references cited). It acts just as an usual acid scavenger, but not as an acid scavenger in the sense of a neutralizer for the antagonism of Sandostab® P-EPQ and HALS.

Example 5

Specimens: A typical LLDPE film grade, a copolymer of ethylene with octene, having a density of 0.920 g/cm³ and a MFI (190°C, 2.16 kg) = 1.0 g/10 min

UV Exposure: Atlas WOM 65 WRC under CAM 7 conditions

Test Criteria: Time to failure by 50% loss of the original elongation at break, i.e. of the maximal elasticity of the films

Formulations: All samples contain as base stabilizers for the tests 0.07% Irganox® 1076 and 0.15% Sanduvor® 3944 plus further additives as listed below

No.	Further Additives	t ₅₀	Relative
A)	0.10% P-EPQ 0.10% CaSt ₂	2567 h	100%
B)	0.10% P-EPQ 0.05% NaSt	3160 h	123%
C)	0.10% P-EPQ 0.15% NaSt	3135 h	122%
D)	0.10% P-EPQ 0.00% NaSt	2494 h	97%
E)	0.10% U-626 0.10% NaSt	2888 h	113%

This series of tests shows, moreover, that the present invention is equally valid for polyethylene. It confirms the results described already in Example 3, emphasizing the

preferred ratios of Sandostab® P-EPQ to sodium stearate of 3/1 to 1/7, most preferred in the range of 2/1 to 1/2 when used in full additive packages for UV stabilized plastic articles. The example E) containing Ultrinox 626 as comparison to Sandostab® P-EPQ is mentioned as one additional reference. This product is known, as is the aforementioned Irgafos® 168, not to reduce the effectiveness of HALS UV stabilized plastics (see EP 0 553 498 A2 and W.O. Drake, K.D. Cooper "Recent Advances in Processing Stabilization of Polyolefins", especially Figure 21 therein). Even such beneficial results can be further exceeded if formulations, such as No. B) and C) are specifically designed as described in the invention.

Example 6

Specimens: Films of 100 µm thickness made by compression molding of a high-molecular-weight type of polypropylene with a MFI (230°C, 5.0 kg) = 1.3 g/10 min, respectively a MFI (230°C, 2.16 kg) = 0.4 g/10 min

UV Exposure: UVCon UVA weathering equipment

Test Criteria: Time to failure by COI = 0.3, designated as "t_f"

Formulations: All samples are base stabilized with 0.05% Irganox® 1010 and 0.15% Sanduvor® 3944 plus further additives as listed below

No.	Further Additives	t _f	Relative
A)	0.07% P-EPQ 0.10% CaSt ₂	805 h	100%
B)	0.07% I-12 0.10% CaSt ₂	807 h	100%
C)	0.07% I-168 0.10% CaSt ₂	1056 h	130%

D)	0.07% P-EPQ 0.10% ZnO	1098 h	136%
E)	0.07% I-12 0.10% ZnO	1061 h	132%
F)	0.07% P-EPQ 0.05% ZnSt ₂ 0.05% ZnO	1025 h	127%
G)	0.07% I-12 0.05% ZnSt ₂ 0.05% ZnO	1022 h	127%

This series of tests shows that the present invention can be extended also to the use of Irgafos® 12 in additive formulations for UV stabilized plastics. Despite its excellent hydrolysis resistance, which is even superior to that of Irgafos® 168 (see lecture of W.O. Drake and K.D. Cooper, both of Ciba-Geigy: "Recent Advances in Processing Stabilization of Polyolefins" presented on February 21-24, 1993, page 419 and Figure 23), Irgafos® 12 exhibits the same negative interaction with HALS compounds as does Sandostab® P-EPQ. However, specific combinations with neutralizers of said antagonism allow the use of Irgafos® 12 also in UV stabilized plastics, provided that these plastic additives are formulated according to the invention.

The inventive formulations containing Sandostab® P-EPQ and Irgafos® 12, respectively, in combination with further additives enable already the producer of the polymer, the compounder or the manufacturer of finished plastic articles to take advantage of both, the unique effectiveness of high performance processing stabilizers and the unlimited state-of-the-art efficiency of HALS compounds for use in a broad variety of UV protected polymers.

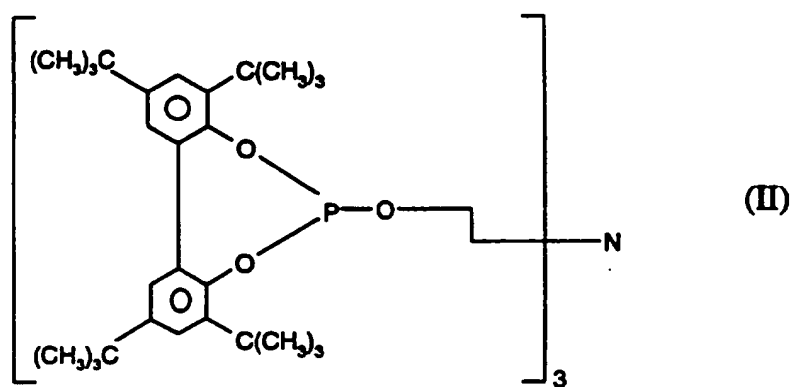
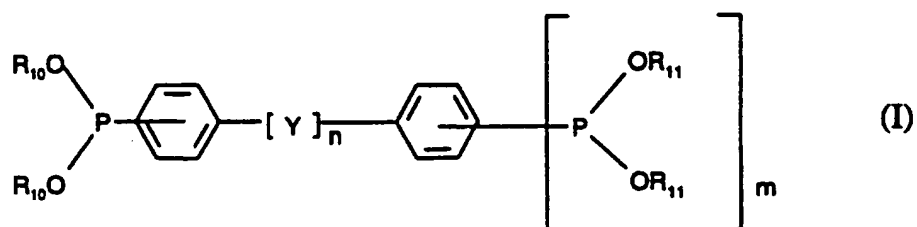
Furthermore, the testing series of Example 6 indicates by the formulations D) and E) clear advantages for combining Sandostab® P-EPQ, respectively Irgafos® 12, preferably with ZnO (French process type of zinc oxide, supplied e.g. by Saint Joe

Company, Monica, PA, USA, Seido Chem. Ind. Co., Osaka, Japan or others) in UV stabilized polyethylenes. Combinations of ZnO with ZnSt₂ (commercially available zinc stearate for polyolefins) and Sandostab® P-EPQ, respectively Irgafos® 12, as listed in formulations F) and G) show also significant improvements over the corresponding references A) and B), respectively, in UV stabilized polyethylenes, formulated according to the invention.

Claims

1. A stabilizer composition comprising

- a) at least one processing stabilizer selected from the group consisting of phosphite, monophosphonites and diphosphonite compounds of formula I or II



in which

m is 0 or 1;

n is 0 or 1;

each R₁₀ and each R₁₁, independently, is an aliphatic, alicyclic or aromatic

group of C_{1-24} carbon atoms, optionally further substituted (for example by linear or branched aliphatic groups or alkaryl substituents) (hereinafter defined as the monovalent significances of R_{10} or R_{11} , respectively);

or both groups R_{10} and/or R_{11} form a cyclic group with a single phosphorus atom (hereinafter defined as the divalent significances of R_{10} or R_{11} , respectively);

Y is -O-, -S-, -CH(R_{15})- or -C₆H₄-,

where R_{15} is hydrogen or C₁₋₈alkyl or COOR₆ and R₆ is C₁₋₈alkyl.

b) at least one acid scavenger selected from the group consisting of sodium stearate, magnesium stearate, zinc stearate; magnesium or magnesium/zinc hydrotalcites, optionally coated with 5 to 50% of metal stearate; zinc oxide, zinc hydroxide, calcium oxide, calcium hydroxide, magnesium oxide, magnesium hydroxide.

c) at least one UV stabilizer selected from compounds containing at least one 2,2,6,6-tetraalkylpiperidinyl-group

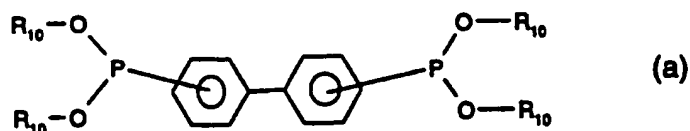
and

d) optionally at least one sterically hindered phenolic antioxidant selected from the group consisting of octadecyl-3-(3',5'-di-tert.-butyl - 4'-hydroxyphenyl)propionate, tetrakis [methylene-3-(3',5'-di-tert.-butyl-4'-hydroxyphenyl) propionate] methane, 1,3,5-trimethyl-2,4,6-tris(3,5-di-tert.butyl-4-hydroxyphenyl)benzene, 1,3,5-tris(3,5-di-tert.-butyl-4-hydroxyphenyl)-1,3,5-triazine-2,4,6-(1H,3H,5H)trione and tris [3,5-di-tert-butyl-4-hydroxybenzyl]isocyanurate.

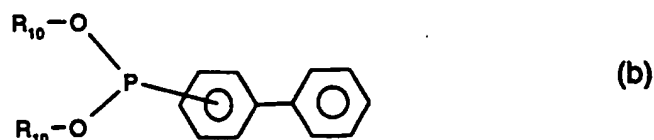
2. A composition according to claim 1 in which the weight ratio of component a) to

b) is from 3:1 to 1:7, preferably from 2:1 to 1:2.

3. A composition according to claim 1 or 2 in which component a) is a mixture of
- i) 50-80% of a diphosponite of the formula (a)



- ii) 5-25% of a monophosponite of formula (b)



- iii) 5-25% of a phosphite of formula (c)



in which each R_{10} is 2,4-di-tertiary butyl phenyl; and where the percentages are weight percentages (based on the sum of the compound of formulae (a), (b), and (c) being 100%).

4. A solid masterbatch composition comprising 10 to 80% by weight, preferably 15 to 40% by weight, of a stabilizer composition according to any preceding claim 1 to 3 and 90 to 20% by weight, preferably 85 to 60% by weight, of a polymeric material which is identical or compatible with the polymeric material to be

stabilized.

5. A liquid concentrate comprising 10 to 80% by weight of a stabilizer composition according to any preceding claim 1 to 3 and 90 to 20% by weight of a solvent.
6. Use of a stabilizer composition according to claim 1 or a solid masterbatch composition according to claim 4 or of a liquid concentrate according to claim 5 as a stabilizer in polymeric materials selected from the group consisting of homopolyolefins and copolyolefins produced in the presence of a so-called generation II or higher catalyst (not subjected to a catalyst removal step after the polymerization process) and mixtures or blends thereof or with other polymers.
7. Use according to claim 6 in which the polyolefin is selected from the group consisting of homopolypropylene, copolypropylene, homopolyethylene, copolyethylene and mixtures or blends thereof or with other polymers.
8. Process for stabilizing polymeric materials selected from the group consisting of homopolyolefins and copolyolefins produced in the presence of a so-called generation II or higher catalyst (not subjected to a catalyst removal step after the polymerization process), and mixtures or blends thereof or with other polymers comprising adding to the polymeric material a stabilizing quantity of a stabilizing composition according to any preceding claim 1 to 3.
9. Process according to claim 8, in which the polyolefin is selected from the group consisting of homopolypropylene, copolypropylene, homopolyethylene, copolyethylene and mixtures or blends thereof or with other polymers.
10. A stabilized polymeric material comprising of
 - a) a stabilizing composition according to any preceding claim 1 to 3
 - and
 - b) a polymeric material selected from the group consisting of homopolyolefins

and copolyolefins produced in the presence of a so-called generation II or higher catalyst (not subjected to a catalyst removal step after the polymerization process) and mixtures or blends thereof or with other polymers.

11. A stabilized polymeric material according to claim 10 in which the polyolefin is selected from the group consisting of homopolypropylene, copolypropylene, homopolyethylene, copolyethylene and mixtures or blends thereof or with other polymers.



Application No: GB 9520193.5
Claims searched: 1 to 11

Examiner: Miss M. M. Kelman
Date of search: 11 December 1995

Patents Act 1977
Search Report under Section 17

Databases searched:

UK Patent Office collections, including GB, EP, WO & US patent specifications, in:

UK CI (Ed.N): C3K KCZ

Int CI (Ed.6): C08K 5/00, 5/3435, 13/00, 13/02, 13/06, 13/08

Other: ONLINE:PATENTS

Documents considered to be relevant:

Category	Identity of document and relevant passage	Relevant to claims
Y	GB 2265377 A SANDOZ see claim 1 and pages 14 to 18	4,5,6,7
Y	GB 2261667 A SANDOZ see pages 13 to 17 and the Example	4,5,6,7
X,P	WO 95/19391 A1 EXXON 20 July 1995 see the claims, page 5, line 23, to page 6, line 1, page 13, lines 19 to 23, and pages 15 and 16	1,3,6 to 11
X,Y	US 4857230 A MATSUMURA see the claims and columns 1 to 3	X:1,2 Y:4,5,6,7

X Document indicating lack of novelty or inventive step
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A Document indicating technological background and/or state of the art.
P Document published on or after the declared priority date but before the filing date of this invention.
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